Summary Progress Report

Application of the MOE TAGA 3000 System to PCB Monitoring Tasks

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Ontario
Ministry of the Environment

The Honourable
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SUMMARY PROGRESS REPORT

APPLICATION OF THE MOE TAGA 3000 SYSTEM TO PCB MONITORING TASKS

PREPARED FOR AND
REVIEWED BY

ONTARIO MINISTRY OF THE ENVIRONMENT
AIR RESOURCES BRANCH
UNDER CONTRACT NO. A60589

ARB-TDA-22-80

BY

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SCIEX Contract No. 101.2

March 27, 1980

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1.0 SUMMARY AND CONCLUSIONS

In brief summary, the MOE TAGA 3000 can analyse PCBs in the cement kiln stack gases with a degree of sensitivity well below the safety limit of 20 micrograms per cubic meter as set out in the Protocol.

This summary progress report has been prepared to update the reader on a number of confirmatory tests that have been carried out at the St. Lawrence Cement plant since the last report of January 21, 1980. In these confirmatory tests, known amounts of PCBs were introduced through a heated injector at the three injection ports along the sampling line. The injected PCBs were transmitted with a 100% efficiency, within experimental uncertainty, to the MOE TAGA 3000. The total minimum detectability for all vaporized PCBs measured is approximately 8.5 micrograms per cubic meter in the stack gas or less for PCBs injected into the sampling system. These results can be compared with the 20 micrograms per cubic meter safety point described in the protocol. The detectability limits combined with the (typically) 120 second measured system response, and good filtering and transmission characteristics of the sampling line, lead us to conclude that the total system is capable of real-time monitoring of PCB destruction at St. Lawrence Cement.

2.0 INTRODUCTION

The first summary progress report* dealt with the capability of the TAGA TM 3000 system for detecting PCBs in ambient air and the preliminary stack simulation studies carried out at SCIEX INC. Based upon the simulation studies, the stack sampling transfer line was constructed at St. Lawrence Cement plant in Mississauga.

The second summary progress report** described the performance of the sample transfer line and the system's response to background chemicals and injected PCBs. Briefly it was shown that vaporized PCBs can be detected in a linear and reproducible fashion when injected into a diluted stack gas through a heated injector. The latter is located downstream of the quartz filter, injection port two (IP2). The filter itself is located approximately 50 cm downstream of the kiln duct and is designed to remove particulate matter greater than ten (10) microns from the stack gas. It was also shown in the report that PCBs injected upstream of the filter (IP3) were not retained on the filter elements or the dust loading to any significant degree. The filter assembly and dust loading were extracted and analyzed by the Laboratory Services Branch of the Ontario Ministry of the Environment using solvent extraction and gas chromatography analysis. Finally, it was reported that the total minimum detectability for all vaporized PCBs of interest (mono- to hexachlorobiphenyl) was approximately 1.5 micorgrams of total PCBs

* SUMMARY PROGRESS REPORT: APPLICATION OF THE MOE TAGA TM 3000 SYSTEM TO PCB MONITORING TASKS, prepared for Ontario Ministry of the Environment, Air Resources Branch, September 10, 1979.

** SUMMARY PROGRESS REPORT: APPLICATION OF THE MOE TAGA TM 3000 SYSTEM TO PCB MONITORING TASKS, prepared for Ontario Ministry of the Environment, Air Resources Branch, January 21, 1980.

per cubic meter of stack gas, which is below the specified safety point of 20 micrograms of total PCBs per cubic meter described in the Protocol*.

Since the last hearing of January 23, 1980, a number of confirmatory tests have been carried out at the St. Lawrence Cement plant. Known amounts of PCBs were introduced through a heated injector at the three injection ports (IP1, IP2, IP3). The PCBs transmitted through the line were detected and quantitated with the MOE TAGA TM 3000. These experiments are dealt with in Section 3 below. Since the stack heating methodology and capability has been completed, some recent work has been done to improve and update the capabilities of the MOE TAGA TM for direct analysis of PCBs in ambient air. These developments are presented in Section 4.

3.0 PROGRESS IN THE 'STACK GAS MONITORING' MODE

3.1 Introduction

The confirmatory tests run on the stack sampling line and the system's response consisted of (a) the transmission of PCBs across the quartz filter assembly, (b) time response test of the total system, (c) total system response to individual PCBs, and (d) the system's response to a mixture of PCBs injected through the three sampling ports - PCB budget along the sampling line. These experiments will be discussed in that order

* PROTOCOL FOR THE INCINERATION OF POLYCHLORINATED BIPHENYLS AT ST. LAWRENCE CEMENT LTD., MISSISSAUGA. Prepared by Air Resources Branch, Ontario Ministry of the Environment, August 1979.

3.2 PCB Transmission Across the Quartz Filter

The sampling line as already reported, is operated at a temperature of 120°C and thus the trapped particulate matter on the quartz filter and elements are kept at this elevated temperature to minimize any retention of PCBs. It has been shown in the second summary progress report that PCBs injected upstream of the filter (IP3) were not retained by the dust loading or filter assembly to a significant degree. The analysis was done by solvent extraction and gas chromatographic analysis, but in view of the nature of the overall performance of the TAGA and the sampling system, this conclusion was confirmed by the use of the MOE TAGA TM itself.

Using this same stack sampling and gas dilution system as in the second progress report, the TAGA system was stabilized by establishing steady background readings for the mass spectral region from mono- to hexa-chlorobiphenyl species. A standard solution containing known amounts of the PCB species was injected downstream of the quartz filter (IP2). The system was then returned to background monitoring to ensure that no residual PCBs were left in the sampling line. The standard solution was then identically injected upstream of the quartz filter (IP3). If any PCBs were retained by the filter assembly or dust loading, the response of the TAGA system would be lower for injections at IP3 than injections at IP2.

Figure 3.1 lists the total responses obtained by injecting the PCBs at IP2, IP3 and composite background readings taken before, between and after the injections. The standard deviations, S_1, S_2, S_3 and S', are the statistical measures of variability that apply to the responses. The S' for each PCB was calculated by the Pooled Variance Method, and indicates the degree of overall standard deviation. The last column in Figure 3.1 shows that any PCB species injected upstream of the filter (IP3) was completely transmitted through the filter (within acceptable experimental uncertainty). This confirms

Figure 3.1

Transmission of PCBs Across Quartz Filter. The parameter m/z, $\bar{x}$ and n denote the mass to charge ratio, the average response and number of observations, respectively. The s parameters are the statistical standard deviations.

SPECIES	M/Z	Equivalent Concentration (ug/m^3)	Response at IP2 Downstream of Filter (ions)		Response at IP3 Upstream of Filter (ions)		Component Background (ions)		Overall (s')	Transmission (%)*
			$\bar{x}$ (n = 3)	s_1	$\bar{x}$ (n = 5)	s_2	$\bar{x}$(n=8)	s_3		
Mono	188	10.2	5562	520	6088	1269	1441	154	808	109.4 ± 14.5 (%)
Di	222	6.9	4414	127	4822	614	1398	85	379	109.2 ± 8.6
	224	6.9	2953	62	3207	268	1172	101	180	109.2 ± 6.0
Tri	256	9.8	5266	91	5036	535	1717	263	378	95.6 ± 7.2
	258	9.8	4692	131	4539	574	1434	184	491	96.7 ± 10.5
Tetra	290	12.6	825	82	876	92	238	72	87	106.2 ± 10.5
	292	12.6	1091	113	1143	151	323	108	133	104.8 ± 12.1
Penta	324	10.5	1440	218	1435	139	648	189	195	99.7 ± 13.5
	326	10.5	2065	302	2109	254	826	299	308	102.1 ± 14.9
Hexa	360	23.7	1445	114	1355	76	633	141	128	93.8 ± 8.9
	362	23.7	1501	153	1366	69	634	155	143	91.0 ± 9.5

* Obtained by

$$100(\%) - \frac{\text{Response (IP2)} - \text{Response (IP3)}}{\text{Response (IP2)}} \times 100(\%) =$$

$$\text{Range} = \frac{s'}{\text{Response (IP2)}} \times 100\ (\%)$$

the analytical results obtained earlier by the Ministry's Laboratory Services Branch.

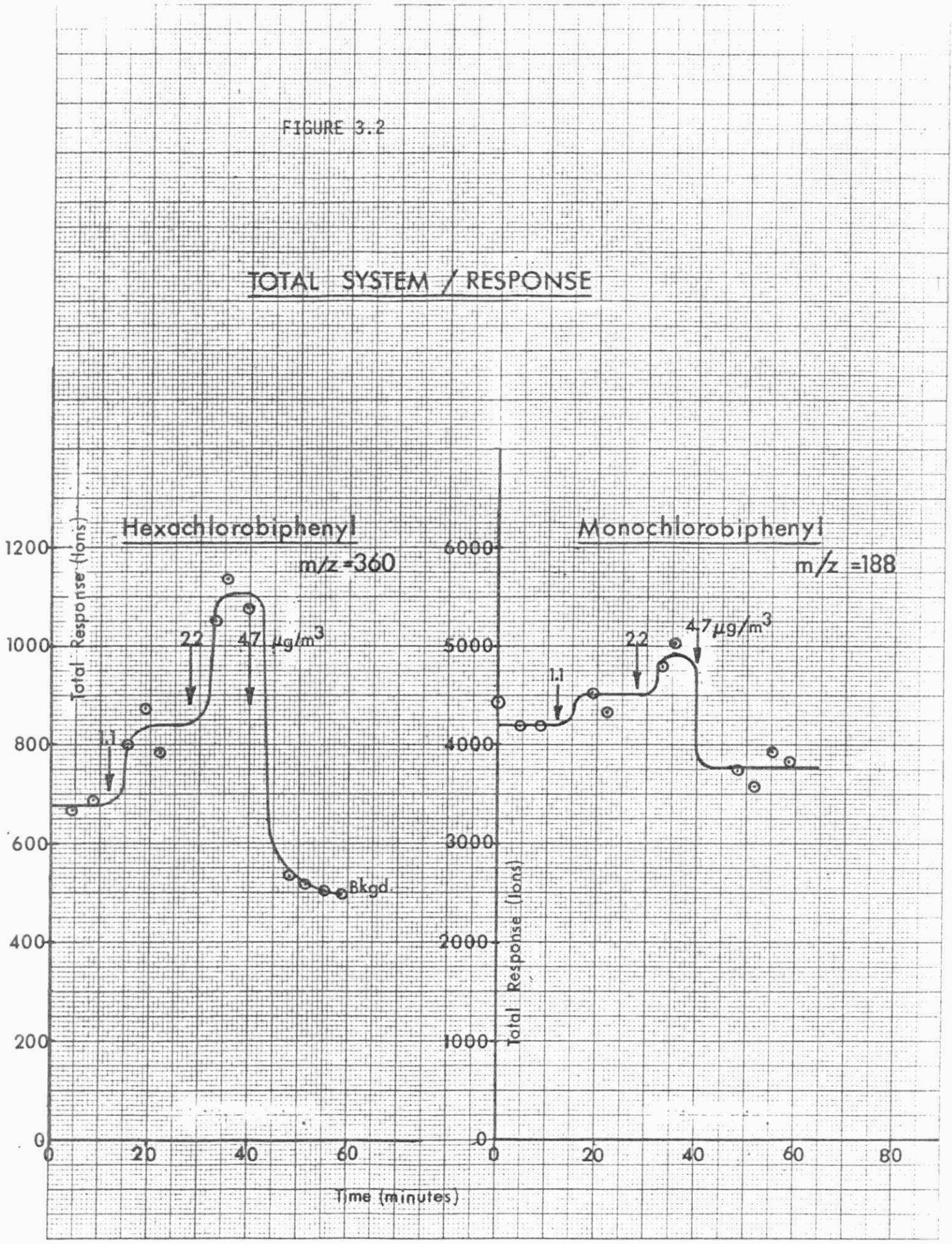
3.3 Time Response Test of the Total System

In the last report it was shown that separate injections downstream of the filter (IP2) of monochlorobiphenyl and hexachlorobiphenyl lead to very rapid signal rise and that fast decay of the signal occurred when injections were halted. This demonstrates that wall effects downstream of the filter assembly have been virtually eliminated. It is advantageous to prove the same effect for the total sampling line (including the filter assembly) by repeating the experiment using the injection port upstream of the filter (IP3). The same experimental procedures were used as reported earlier. Figure 3.2 shows a plot of the TAGA TM response against time when monochlorobiphenyl and hexachlorobiphenyl were individually injected into the gas stream at IP3. The results confirm our earlier conclusion from experiments with injections at IP2.

3.4 Total System Response to PCBs

In the last progress report, the system's response to PCBs was reported for experiments where injections of known amounts to PCBs were done downstream of the filter (IP2). The overall results showed a good linear response, high sensitivity and low detection limits (4.0 - 5.3 micrograms per cubic meter of total PCBs). Subsequent to the last report, these experiments have been repeated using the same procedure as in the last progress report with the injections of PCBs upstream of the filter (IP3). These experiments were conducted to test and validate the total system's response including the quartz filter and cement dust loading.

FIGURE 3.2



46 1510
10 X 10 TO THE CENTIMETER 18 X 25 CM.
KEUFFEL & ESSER CO MADE IN U.S.A.
K+E

The experimental results have been analyzed using a statistical computer program, "The Least-Squares Method of Curve Fitting", where the TAGA TM response and the concentration of added PCBs are fitted to a mathematical equation representing the structural relationship between the two variables. This procedure has been described in detail in the Appendices of the previous progress reports.

Figures 3.3, 3.5, 3.7, 3.9, 3.11 and 3.13 show the TAGA's total response to the individual PCBs injection into the diluted stack gas upstream of the filter (IP3). The responses are expressed in number of ions and the concentration of injected PCBs in micrograms per cubic meter of the stack gas. The slope is the total system's sensitivity in terms of (ions)/(ug/m^3). The intercept indicates the total system's response by statistics when no PCBs are added. The correlation co-efficient (CORR.COEFF.) is a measure of the linearity between the total system's response and the PCB concentrations (1.000 being a perfectly linear response).

Figures 3.4, 3.6, 3.8, 3.10, 3.12 and 3.14 show in graphical form the total system's response to the individually injected PCB species (monochlorobiphenyl to hexachlorobiphenyl, inclusive). The two most abundent isotope peaks (except monochlorobiphenyl) were monitored for each PCB species containing an equal number of chlorine atoms. The detection limits of the instrument were determined from the curves for each PCB species. It is to be noted that the detection limit is defined as being 3s, where s is the standard deviation calculated from the set of repeated measurements of the background signal taken before the injection of the known amounts of PCBs at each mass-to-charge position of interest. This has been given in detail in the previous report.

Figure 3.15 summarizes the overall results. The figure also shows that the correlation coefficients between (a) the equivalent concentration and the total system's response are in the range

Figure 3.3

MONOCHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER

TOTAL RESPONSE VS CONCENTRATION

ROW	1(188)	2($\mu g/m^3$)
1	3820	0
2	3927	0
3	3570	0
4	3747	0
5	4625	4.763
6	5015	4.763
7	4774	4.763
8	6363	1.201
9	5769	10.201
10	6053	10.201
11	7607	19.406
12	8077	19.406
13	7904	19.406
14	4195	1.082
15	4199	1.082
16	4424	1.082
17	4312	2.217
18	4537	2.217
19	4388	2.217

FOR COLUMN 1 VERSUS COLUMN 2

SLOPE 192.916
INTERCEPT 4065.33
CORR.COEF 0.927961

3s	Detection Limit
450.4	2.335 ug/m^3

Figure 3.4

PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT(UPSTREAM OF FILTER)
(February 18, 1980)

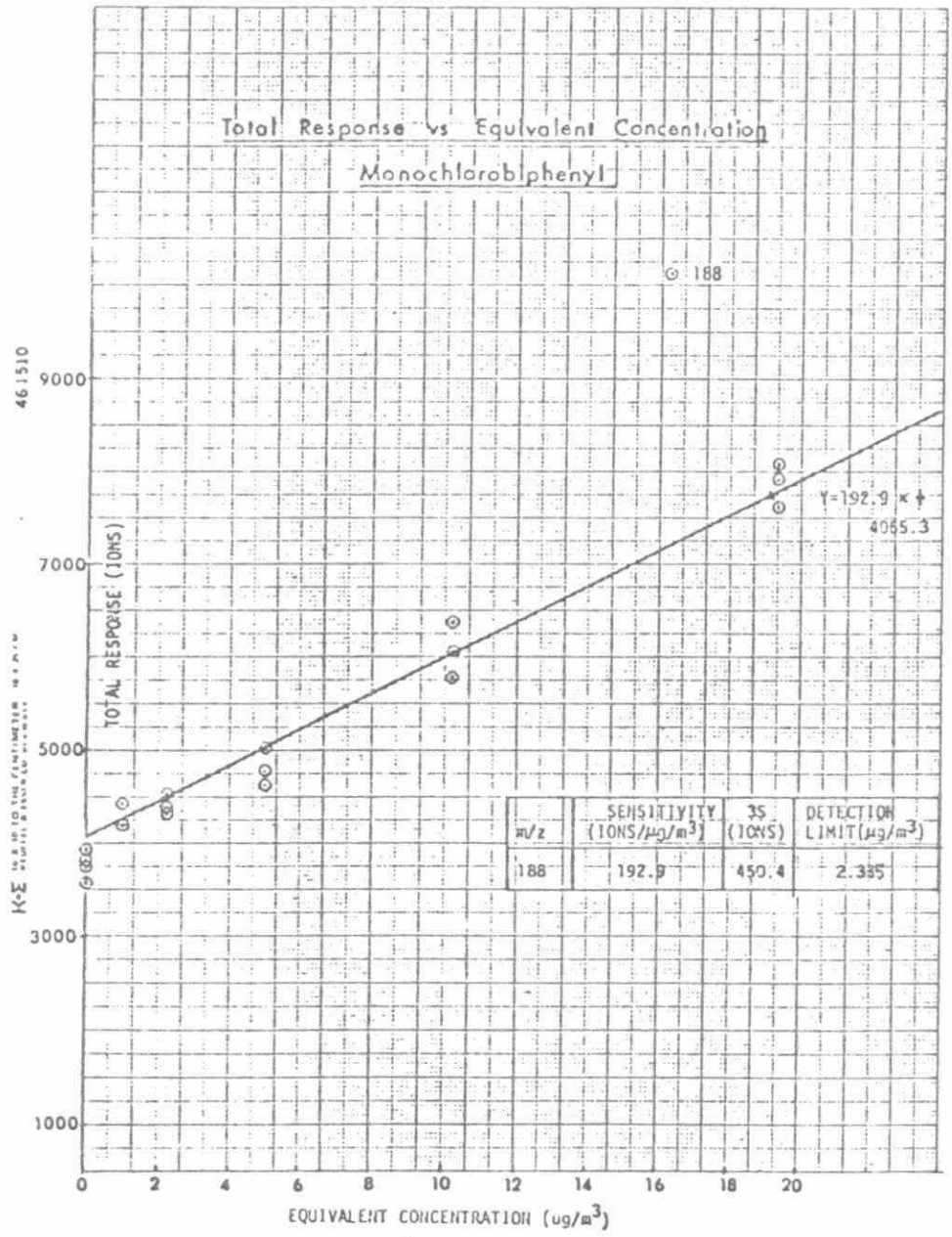


Figure 3.5

DICHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER

TOTAL RESPONSE VS CONCENTRATION DICHLOROBIPHENYL

ROW	1 (222)	2 (224)	3 ($\mu g/m^3$)
1	3075 ions	2685 ions	0
2	3310	2664	0
3	3213	2588	0
4	3566	2830	0
5	3884	2946	3.228
6	4185	3278	3.228
7	3953	3105	3.228
8	4452	3451	6.914
9	4547	3903	6.914
10	4719	3706	6.914
11	5908	4388	13.151
12	5976	4335	13.151
13	5639	4178	13.151

FOR COLUMN 1 VERSUS COLUMN 2

SLOPE 1.4959
INTERCEPT-735.063
CORR.COEF 0.980351

FOR COLUMN 1 VERSUS COLUMN 3

SLOPE 191.559
INTERCEPT 3304.09
CORR.COEF 0.986459

FOR COLUMN 2 VERSUS COLUMN 3

SLOPE 124.015
INTERCEPT 2722.38
CORR.COEF 0.974491

m/z	3s	Detection Limit
222	622	3.247 ug/m^3
224	303	2.443 ug/m^3

Figure 3.6

PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT(UPSTREAM OF FILTER)
(February 18, 1980)

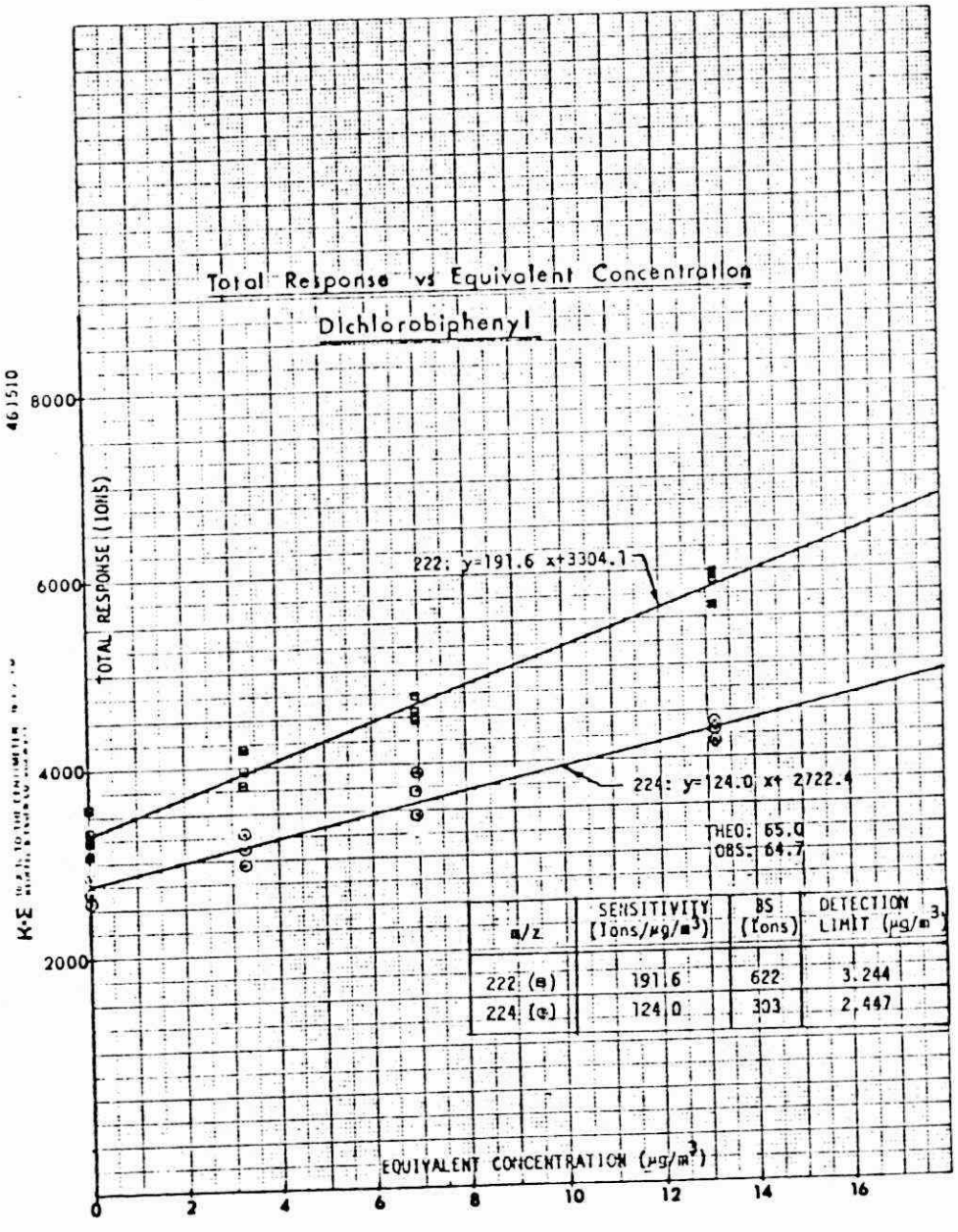


Figure 3.7

TRICHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER

TOTAL RESPONSE VS CONCENTRATION

ROW	1 (256)	2 (258)	3 (ug/m^3)
1	1357	1239	0
2	1387	1293	0
3	1340	1296	0
4	1337	1317	0
5	2302	2096	4.553
6	2319	2158	4.553
7	2197	2071	4.553
8	3083	2837	9.751
9	3011	2763	9.751
10	2958	2875	9.751
11	4418	4263	18.549
12	4704	4462	18.549
13	5038	4639	18.549
14	1765	1626	1.033
15	1637	1602	1.033
16	1661	1589	1.033
17	1840	1719	2.119
18	1877	1737	2.119
19	1808	1657	2.119

FOR COLUMN 1 VERSUS COLUMN 2

SLOPE 1.06169
INTERCEPT 6.96893
CORR.COEF 0.998601

FOR COLUMN 1 VERSUS COLUMN 3

SLOPE 175.353
INTERCEPT 1426.22
CORR.COEF 0.993374

FOR COLUMN 2 VERSUS COLUMN 3

SLOPE 165.324
INTERCEPT 1335.87
CORR.COEF 0.99573

m/z	3s	Detection Limit
256	68.8	0.392 ug/m^3
258	99.8	0.604 ug/m^3

Figure 3.8

PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT(UPSTREAM OF FILTER)
(February 18, 1980)

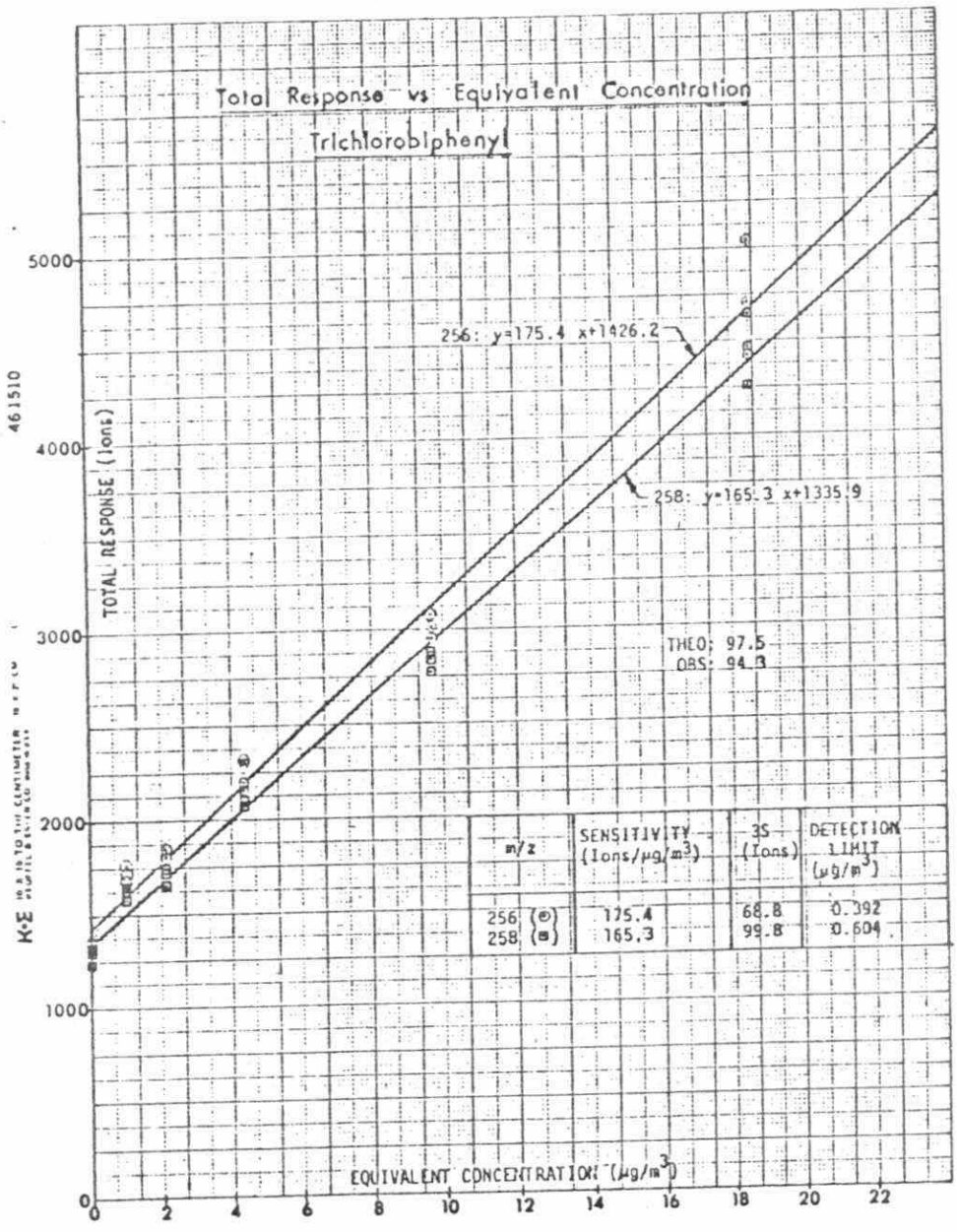


Figure 3.9

TETRACHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER

TOTAL RESPONSE VS CONCENTRATION

ROW	1 (290)	2 (292)	3($\mu g/m^3$)
1	121	136	0
2	150	181	0
3	145	187	0
4	162	181	0
5	390	475	5.888
6	363	442	5.888
7	364	492	5.888
8	551	648	12.611
9	455	554	12.611
10	481	645	12.611
11	871	1018	23.99
12	899	1171	23.99
13	993	1226	23.99
14	224	266	1.337
15	205	238	1.337
16	201	243	1.337
17	276	291	2.74
18	256	312	2.74
19	266	304	2.74

FOR COLUMN 1 VERSUS COLUMN 2

SLOPE 0.792047
INTERCEPT 12.4553
CORR.COEF 0.996079

FOR COLUMN 1 VERSUS COLUMN 3

SLOPE 30.9015
INTERCEPT 160.848
CORR.COEF 0.988136

FOR COLUMN 2 VERSUS COLUMN 3

SLOPE 38.7887
INTERCEPT 189.016
CORR.COEF 0.986276

m/z	3s	Detection Limit
290	51.6	1.671 ug/m^3
292	71.0	1.831 ug/m^3

Figure 3.10

PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT(UPSTREAM OF FILTER)
(February 18, 1980)

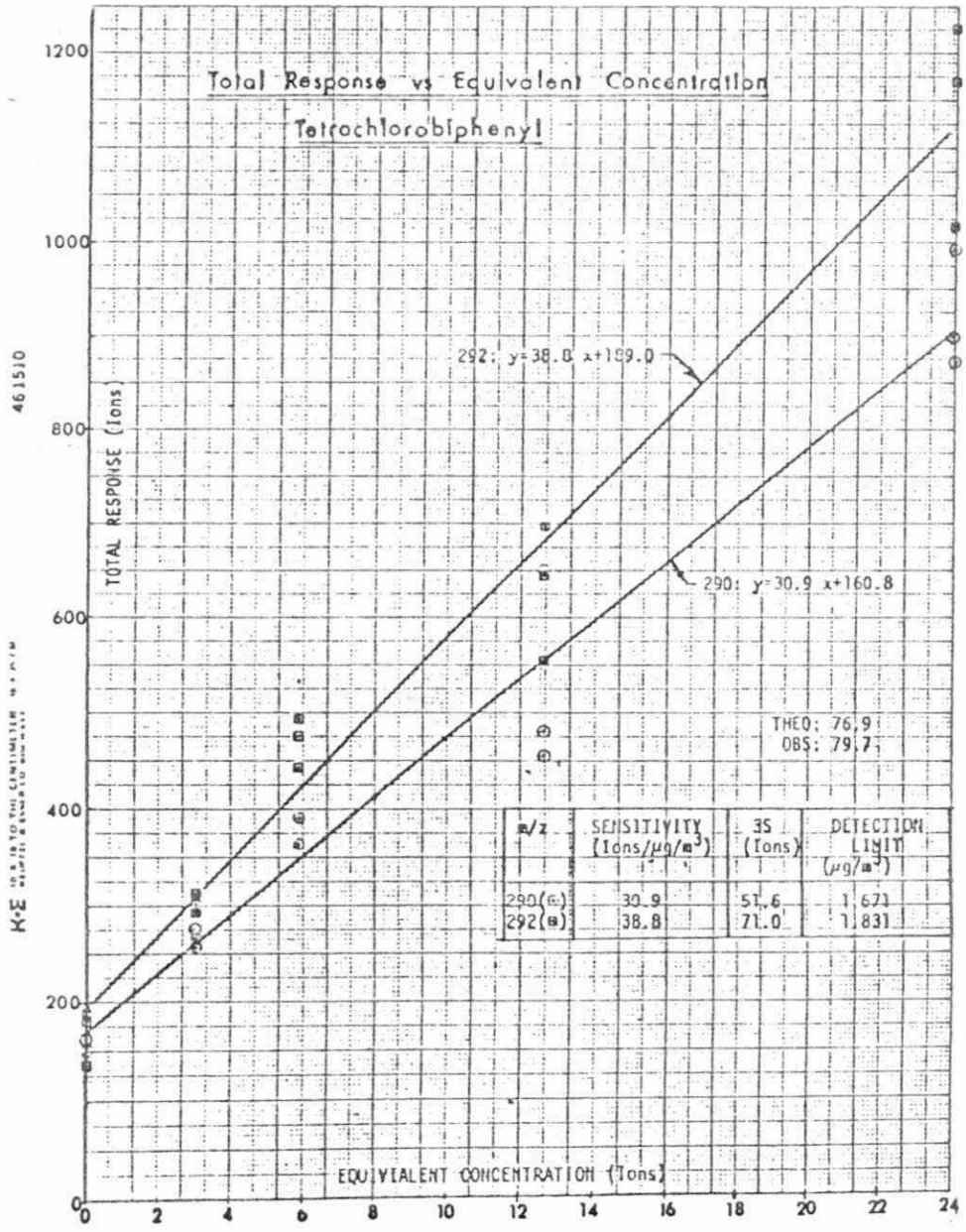


Figure 3.11

PENTACHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER

TOTAL RESPONSE VS CONCENTRATION

ROW	1(324)	2(326)	3($\mu g/m^3$)
1	456	329	0
2	476	366	0
3	485	371	0
4	490	383	0
5	1005	1075	4.921
6	919	993	4.921
7	945	1030	4.921
8	1313	1634	10.539
9	1241	1459	10.539
10	1261	1556	10.539
11	1986	2563	20.048
12	2091	2818	20.048
13	2222	3152	20.048
14	659	516	1.117
15	641	497	1.117
16	567	480	1.117
17	690	607	2.29
18	690	645	2.29
19	703	586	2.29

FOR COLUMN 1 VERSUS COLUMN 2

SLOPE 0.6383
INTERCEPT 284.073
CORR.COEF 0.997822

FOR COLUMN 1 VERSUS COLUMN 3

SLOPE 78.4671
INTERCEPT 509.44
CORR.COEF 0.993754

FOR COLUMN 2 VERSUS COLUMN 3

SLOPE 122.334
INTERCEPT 356.743
CORR.COEF 0.991083

m/z	3s	Detection Limit
324	45.0	0.571 ug/m^3
326	49.9	0.571 ug/m3

Figure 3.12

PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT(UPSTREAM OF FILTER)
(February 18, 1980)

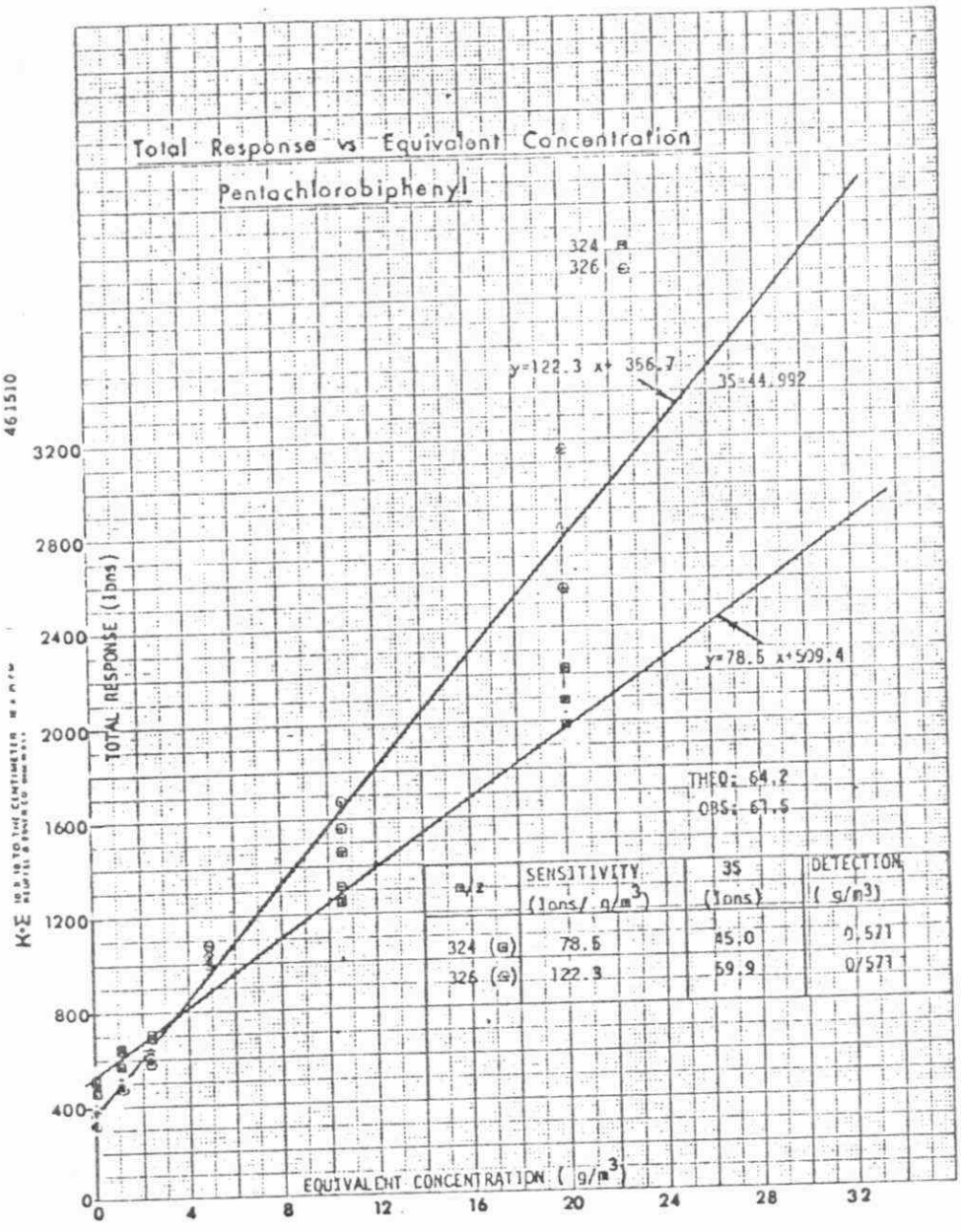


Figure 3.13

HEXACHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER

TOTAL RESPONSE VS CONCENTRATION

ROW	1(360)	2(362)	3(ug/m^3)
1	496	559	0
2	501	598	0
3	518	582	0
4	531	604	0
5	1078	1148	11.051
6	1135	1153	11.051
7	1050	1101	11.051
8	1518	1444	23.668
9	1273	1320	23.668
10	1333	1411	23.668
11	2313	2241	45.023
12	2613	2437	45.023
13	2779	2679	45.023
14	688	770	2.509
15	668	751	2.509
16	679	665	2.509
17	781	800	5.143
18	836	850	5.143
19	301	824	5.143

FOR COLUMN 1 VERSUS COLUMN 2

SLOPE 1.09309
INTERCEPT -125.686
CORR.COEF 0.998101

FOR COLUMN 1 VERSUS COLUMN 3

SLOPE 43.4361
INTERCEPT 536.992
CORR.COEF 0.992999

FOR COLUMN 2 VERSUS COLUMN 3

SLOPE 39.7402
INTERCEPT 606.202
CORR.COEF 0.984948

m/z	3s	Detection Limit
360	48.2	1.109 ug/m^3
362	60.3	1.518 ug/m^3

Figure 3.14

PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT(UPSTREAM OF FILTER)
(February 18, 1980)

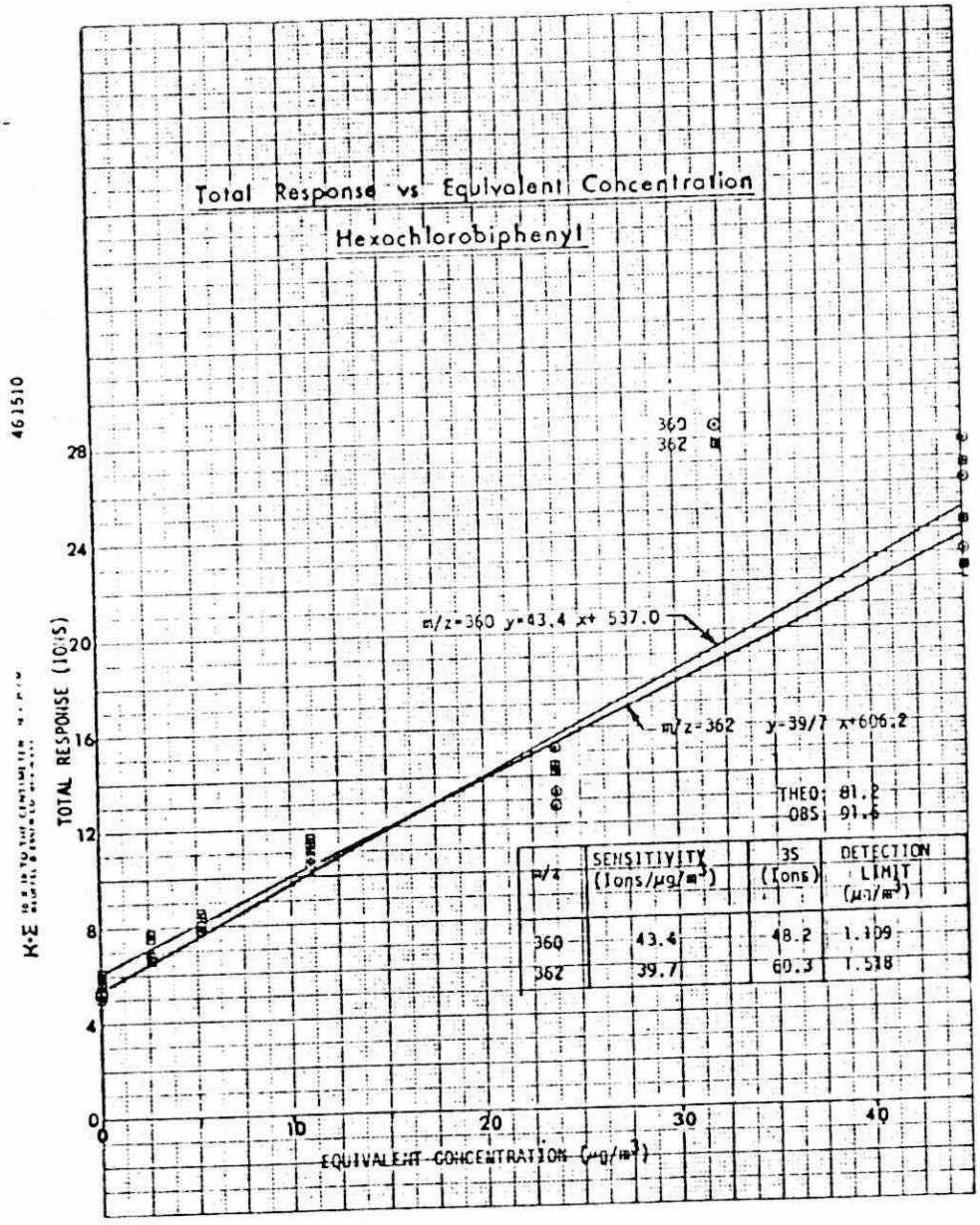


Figure 3.15

SUMMARY OF RESULTS

TOTAL SYSTEM'S RESPONSE TO PCBs INJECTED UPSTREAM OF FILTER

PCB SPECIES	Mono-	Di-		Tri-		Tetra-		Penta-		Hexa-	
mass/charge	188	222	224	256	258	290	292	324	326	360	362
Detection Limits (ug/m^3)	2.335	3.247	2.443	0.392	0.604	1.671	1.831	0.571	0.571	1.109	1.518
Sensitivity (slope) ($ions/ug/m^3$)	192.9	191.6	124.0	175.4	165.3	30.9	38.8	78.5	122.3	43.4	39.7
Observed Isotopic Abundance Ratio (%)		64.7		94.3		79.7		67.5		91.5	
Theoretical Isotopic Abundance Ratio (%)		65.0		97.5		76.9		64.2		81.2	
% Deviation Between Observed & Theoretical Ratios		0.5		3.3		3.5		5.1		11.3	
Corr. Coeff. (response versus concentration)	0.928	0.985	0.974	0.993	0.996	0.988	0.986	0.994	0.991	0.983	0.985
Corr. Coeff. (between isotopes)		0.980		0.999		0.996		0.998		0.998	

of 0.928 - 0.996 and (b) the responses of the two most abundant isotopes of each PCB group is between 0.980 - 0.999. The figure also shows that deviation between the observed and theoretical or expected isotopic ratios are within 5% except for the hexachloro species (11%). These correlations lead to an added confidence in distinguishing between a true PCB response and interfering background peaks. This can further be substantiated by the poor correlations (0.1 - 0.4) when PCBs are not added to the diluted gas stream (more details are given in the Appendix).

In summary, the minimum detectability of the vaporized PCBs in the stack in micrograms per cubic meter with a signal-to-noise ratio of 3:1 are (This signal-to-noise ratio is quite stringent, during the test burn it will be possible to measure with a lower ratio)

PCB Species & Mass Peak						
Mono 188	Di 224	Tri 256	Tetra 290	Penta 324	Hexa 360	"Worst-Case"Minimum Detectability (sum of all Species)
2.335	2.443	0.392	1.671	0.571	1.109	8.521

This "Worst-Case" minimum detection limit for a experiments done that day is slightly higher than the previously reported detection limit when injections were made downstream of the filter. The "Worst-Case" minimum detection limits by the MOE TAGA TM have been observed to fluctuate on a day-to-day basis due to the changing and fluctuating background chemicals (other than PCBs) present in the stack gas and ambient air (used for dilution). None of these minimum detection limits exceeds the safety limit of 20 micrograms per cubic meter specified in the Test Burn Protocol. These results indicate a need to establish the background levels of chemicals on a day-to-day basis during the test burn.

3.5 PCB Budget Along the Sampling Line

Combining the results of PCB injections made at IP1 and IP2

(last Progress report) and the results with injections at IP2 and IP3 (section 3.2 of this report), we have established that PCBs injected at any of the three ports are transferred with approximately a 100% efficiency within experimental uncertainty. However these experiments were performed during different time periods. In order to further confirm the 100% transmission efficiency, PCBs were injected at the three ports, IP1, IP2, and IP3, during one continuous experiment.

The experiments were done using the same procedures described for the separate injections in the previous report and in the previous sections of this report with the exception of two minor improvements in the sampling line; (a) injection port (IP3) has been redesigned (Figure 3.16) to eliminate occasional syringe needle clogging by cement dust; and (b) a heat exchanger with circulating water and a thermostated water bath has been installed upstream of IP1 so that the temperature of the sampled gas can be more accurately cooled from 120^{o}C to 50^{o}C before it reaches the wire integrator. After these modifications, background readings and PCB injections were made at IP1 followed by IP2 and then IP3. The total responses for all experiments were compared in order to derive the PCB transmission coefficients or PCB budget along the line.

Figure 3.17 compares the total system's response when equal amounts of PCBs were injected at IP1, IP2 and IP3 with the composite background. Figure 3.18 shows the transmission efficiency throughout the system. To obtain the results in Figure 3.18, the results in Figure 3.17 were used. The results indicate that the sampling line transports the injected PCBs without any significant loss on the walls or the filter assembly and dust loading (roughly a 100% transmission for all tested PCB species).

FIGURE 3.16

SCHEMATIC OF MODIFIED STACK SAMPLING SYSTEM

TC = THERMOCOUPLE SENSOR
IP = INJECTION PORT FOR MOTORIZED SYRINGE
P = PRESSURE GAUGE
M = MAGNEHELIC GAUGE TO MEASURE FLOW
V = VALVE TO ADJUST FLOW

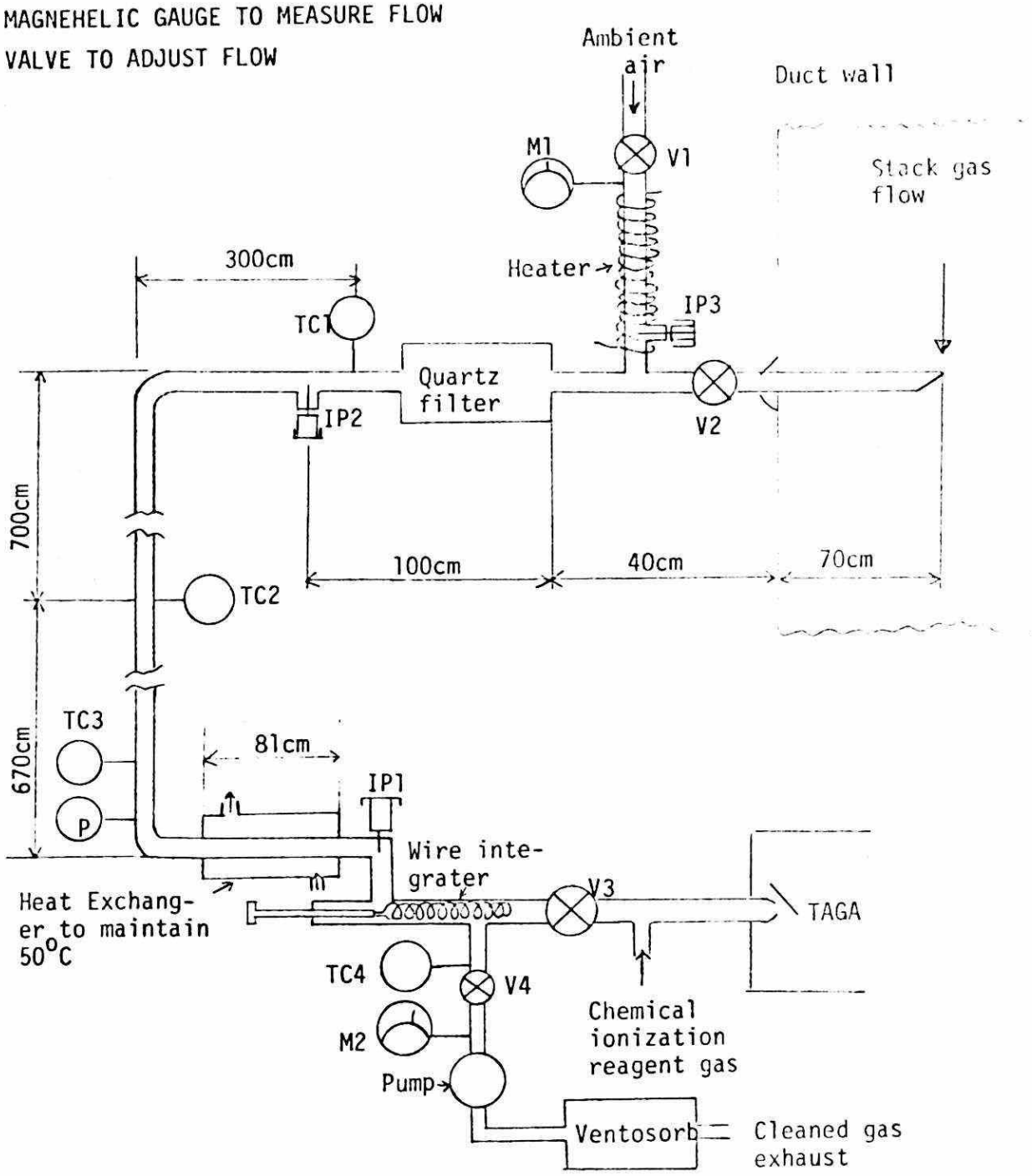


Figure 3.17

Comparison of Total Responses at Different Injection Points

SPECIES		PCB Concn. (ug/m^3)	Total Response Upstream (IP3)		Total Response Downstream (IP2)		Total Response Van (IP1)		Background	
			Av of 3	s_1	Av of 3	s_2	Av of 3	s_3	Av of 4	s_4
Mono	188	1.924	6901	148	7532	242	6888	28	5634	21
Di	222	1.304	11871	149	13653	51	11443	224	8798	160
	224		10291	284	11652	137	9888	34	7794	221
Tri	256	1.840	1878	44	1734	82	1753	63	1042	72
	258		1838	104	1636	77	1756	66	1051	46
Tetra	290	2.379	1030	23	1110	35	1013	34	402	23
	292		1177	61	1320	18	1165	78	435	5
Penta	324	1.988	555	23	650	9	567	24	272	23
	326		589	57	687	21	623	43	206	11
Hexa	360	4.465	1159	59	1269	25	1235	29	566	28
	362		1211	42	1304	25	1223	25	671	24

Figure 3.18

Total PCB Budgeting (% Transmission)

SPECIES	M/Z	VAN	DOWNSTREAM OF FILTER (IP2)	UPSTREAM OF FILTER (IP3)
Mono	188	100 %	109 ± 12 %	100 ± 7%
Di	222	100	119 ± 8	104 ± 8
	224	100	117 ± 12	104 ± 11
Tri	256	100	99 ± 11	107 ± 10
	258	100	93 ± 10	105 ± 12
Tetra	290	100	109 ± 7	102 ± 3
	292	100	113 ± 12	101 ± 7
Penta	324	100	101 ± 8	98 ± 5
	326	100	110 ± 7	95 ± 9
Hexa	360	100	103 ± 5	94 ± 7
	362	100	106 ± 5	99 ± 5

4.0 PROGRESS IN THE "AMBIENT AIR MONITORING" MODE

In the September 10, 1979 Summary Progress Report, we described and implemented a number of improvements to the capability of the MOE TAGA 3000 for ambient air monitoring of PCBs. These improvements lead to detection limits of 4 to 12 nanograms per cubic meter for dichloro- to pentachlorobiphenyls. The hexachlorobiphenyl detection limit was 55 ng/m^3 while the limit for monochlorobiphenyl was not determined due to interferring chemicals other than PCBs. Since the aforementioned report, most of our efforts with the MOE TAGA TM 3000, have been dedicated to developing the required methodology for stack gas monitoring of PCBs. The latter has now been completed as described in the previous sections of this report. Some of the developments for stack testing can be utilized to improve the ambient monitoring capability of the TAGA 3000. SCIEX INC. has recently proposed a Research and Development Programme with the hope of resolving the remaining problems with ambient monitoring of PCBs. The programme is designed to (a) reduce interference problems in the mono-, di-, and hexa-chlorobiphenyls, and (b) develop a source of clean or constant quality air for calibration purposes. This will lead to more reliable and reproducible results than could be achieved with regular ambient air. In order to achieve point (a) above, a series of experiments will be conducted as follows:
(i) the use of the discrimination capability of the newly developed computer software, PCBMON, to optimize the ion optics and the adsorption-desorption characteristics of the PCB wire integrator;
(ii) investigation of alternative reagent ion species (other than benzene) to improve the specificity of the atmospheric pressure chemical ionization; (iii) the optimization of the newly developed multi-purpose front end ionizer through the choice of the optimum position of the corona discharge; and, (iv) investigation of alternative coating materials and operational parameters of the

PCB wire integrator.

The results obtained so far are of a preliminary nature and full details will be submitted at a later date.

5.0 APPENDIX A

Correlation Coefficients

The concept of the linear correlation coefficient, r, has been introduced to the reader at an early stage of this project (see the first Summary Progress Report of September 10, 1979). This statistical term is used as a measure of the linear or proportional association between variables X and Y, of a straight line Y = A + BX. In this formula A and B are constants whose actual numerical values are determined from the observations and certain rules of computation. In other words, this formula expresses the relationship between X and Y, and in this context the linear correlation coefficient measures how well this assumption holds up in the light of the bivariate data set on these two variables. One very often speaks of "fitting" a straight line to the data when computing the particular values of A and B, and in this case the value of r indicates how well the line Y = A + BX "fits" the data. There are several methods to evaluate the degree of association on an objective basis. However, for a subjective evaluation we can use the following guideline:

Numerical Value for r	Evaluation of the Linear Correlation
1.0	Perfect
0.9 to 1.0	Very High
0.8 to 0.9	High
0.6 to 0.8	Moderate
0.5 to 0.6	Poor
0.0 to 0.5	Very Poor
0.0	None

We have been applying this statistical tool to evaluate the analytical data collected by the TAGA TM system. PCBs contain from one to ten chlorine atoms attached to the biphenyl ring system. The element chlorine consists, in nature, of 2 isotopes, that is, 75.8% chlorine-35 and 24.2% chlorine-37. For this reason a PCB species containing n chlorine atoms will give (n+1) mass spectral peaks to represent all the

possible combinations of the chlorine isotopes (see the September report, Appendix). As an example dichlorobiphenyl contains 56.9% of the isotope with 2 chlorine-35 atoms (M/Z = 222), 37.0% of the isotope with one chlorine-35 and one chlorine-37 atoms (M/Z = 224), and the balance (6.9%) of the isotope with 2 chlorine-37 atoms (M/Z = 226). Since these proportions are independent of the atmospheric concentration of PCBs, and the position of chlorine attachments, the response at m/z = 224 increases with an increase at m/z = 222. However, if an increase is not due to PCBs, changes at various PCB isotope positions do not necessarily agree.

When the concentration of PCBs introduced into the TAGA TM system is gradually increased, the system's response should also increase accordingly. This proportional increase between response and PCB concentration has been illustrated a number of times.

Any commercial PCB is a complicated mixture of chlorbiphenyls with different numbers of chlorine atoms per molecule and their isomers. As such, when the environmental concentration of one PCB group containing the same number of chlorine atoms increases, concentrations of other groups will, usually, follow. For instance, an increase of response at m/z = 222 is accompanied by a similar increase at m/z = 256.

In order to demonstrate how well this concept of the linear correlation coefficient works to validate analytical data obtained by the MOE TAGA TM system, a comparison table has been prepared and is shown in Figure 4.19. In this table r values between various PCB peak responses are shown, for instance, r=-0.696 (column 6, row 2) is a correlation coefficient between response at m/z = 224 and m/z = 292, when no PCB was added to the system, and is a poor correlation. The upper right half triangle shows r values when no PCBs were added to the system, whereas those values shown in the bottom left triangle indicate very high to perfect correlations when known amounts of PCBs were added to the system.

It is clear from the table that these correlation coefficients can indicate a degree of confidence in our results.

This statistical treatment can be applied to evaluate the possibility that certain ambient air contains background levels of PCBs before using it to prepare calibration curves, or most importantly, to examine whether the St. Lawrence Cement stack gas contains some un-decomposed PCBs even before any calibration is attempted.

Figure A.1 Comparison of r in the presence and absence of PCBs

	222	224	256	258	290	292	324	326	360	362
222		0.755	-0.381	-0.302	-0.597	-0.452	-0.147	-0.115	-0.721	-0.802
224	0.995		0.165	-0.303	-0.435	-0.696	0.365	0.209	-0.203	-0.754
256	0.999	0.995		0.393	0.262	0.232	0.276	0.797	0.551	-0.046
258	0.997	0.996	0.999		0.674	0.614	0.040	0.742	0.337	0.412
290	0.996	0.994	0.997	0.998		0.333	0.311	0.279	0.611	0.698
292	0.995	0.990	0.996	0.995	0.999		-0.660	0.294	-0.965	0.254
324	0.991	0.987	0.994	0.993	0.997	0.999		0.265	0.759	0.319
326	0.990	0.985	0.993	0.992	0.997	0.999	1.000		0.443	-0.0128
360	0.994	0.989	0.995	0.994	0.998	0.999	0.999	0.999		0.648
362	0.991	0.986	0.993	0.992	0.997	0.999	0.999	0.999	0.999	

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